Reactivity of Early-Transition-Metal Fulvene Complexes. Transformation of a 2,3,4,5-Tetramethylfulvene Ligand into a Bidentate Dialkoxide with Four Asymmetric Carbon Atoms. Molecular Structure of Ti[(OCHPh)2C5Me4(CH2)]Cl2

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the data were corrected for Lorentz and polarization effects. The structures were solved by direct methods (MULTAN)[9] or Patterson methods, and successive cycles of difference Fourier maps followed by least-squares refinement. Scattering factors were taken from ref 10.

1: Monoclinic, space group $P2_1/c$ (No. 14), $Z = 4$; $a = 15.910$ (4), $b = 10.294$ (6), $c = 20.817$ (7) Å; $\beta = 98.63$ (2)°; $V = 3371$ Å^3; d(calcd) = 1.282 g cm^{-3}; $3° < 2\theta < 55°$ (Mo K_α, $\lambda = 0.71069$ Å; $\mu = 25.2$ cm^{-1}). 2: Monoclinic, space group $P2_1/c$ (No. 14), $Z = 4$; $a = 16.118$ (7), $b = 10.398$ (2), $c = 20.996$ (4) Å; $\beta = 98.87$ (3)°; $V = 3477$ Å^3; d(calcd) = 1.495 g cm^{-3}; $3° < 2\theta < 50°$ (Mo K_α, $\lambda = 0.71069$ Å; $\mu = 51.4$ cm^{-1}). Totals of 5919 and 6108 unique reflections were collected at 24 °C for 1 and 3, respectively. Of these, 3035 and 3414 reflections with $I > 3.0\alpha(I)$ were used to solve (direct methods) and refine (full-matrix, least squares) the structures of 1 and 3, respectively. The final R and R_w values were 0.053 and 0.061 for 1 and 0.042 and 0.050 for 3. C13 in the structure of 1 is disordered. There is a 50:50 occupancy of positions C13A and C13B.

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Supplementary Material Available: Tables of bond distances, bond angles, atomic coordinates, and thermal parameters for 1 and 3 (13 pages); listings of structure factor amplitudes for 1 and 3 (33 pages). Ordering information is given on any current masthead page.

Reactivity of Early-Transition-Metal Fulvene Complexes. Transformation of a 2,3,4,5-Tetramethylfulvene Ligand into a Bidentate Dialkoxide with Four Asymmetric Carbon Atoms. Molecular Structure of $Ti[(OCHPh)_2C_5Me_4(CH_2)]Cl_2$

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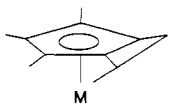
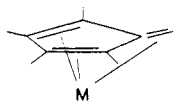
Summary: Cp*FvTiCl (**1**; Cp* = η^5-C_5H_5, Fv = η^6-$C_5Me_4CH_2$) reacts with benzaldehyde, yielding Cp*Ti-$[(OCHPh)_2C_5Me_4(CH_2)]Cl$ (**2**) as the result of insertion in two Ti–C bonds at the 2- and 4-positions of the fulvene ligand in **1**. Complex **2** reacts with HCl to give Cp^*TiCl_3 (**3**) and the corresponding dialcohol and with $TiCl_4$ to give **3** and $Ti[(OCHPh)_2C_5Me_4(CH_2)]Cl_2$ (**5**). X-ray diffraction analysis of **5** shows it to be a dialkoxide–dichloride monomeric titanium complex with a tetrahedral arrangement of the ligands around the metal center. Crystal data for $C_{24}H_{26}Cl_2O_2Ti$: monoclinic, $P2_1/n$, $a = 10.602$ (5) Å, $b = 14.157$ (4) Å, $c = 15.274$ (5) Å, $\beta = 103.76$ (3)°, $V = 2227$ (1) Å^3, $Z = 4$, $R = 0.037$.

The bonding of a tetramethylfulvene ligand to early transition metals has been described as intermediate between the two extremes A and B.[1]



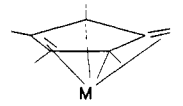
A



B

In complexes of the type Cp*FvM and Cp*FvMCl (M = Ti, Zr) the fulvene ligand reacts with ketones or nitriles, through an adduct intermediate, to give bidentate alkoxide- or amide-functionalized tetramethylcyclopentadienyl groups.[2] This reactivity can be explained in terms of the cyclopentadienyl alkyl structure A. Nevertheless, spectroscopic and structural data for these compounds point to a significant contribution of structure B.[3] A different bonding of the fulvene group is observed in late-transition-metal fulvene complexes, where in some cases the ligand appears to be bonded as a η^4-diene[4] or η^2-olefin[5] and extrusion of the fulvene ligand is observed.[6]

We wish to report here an unprecedented reactivity of this type of ligand that can be well understood in terms of another bonding form, C, a special type of 1,3-diene complex, in which the diene coordinates in a σ^2,π mode as has been observed for a number of Zr and Hf complexes.[7]



C

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Table I. Selected Bond Distances (Å) and Angles (deg) for 5

Bond Distances			
Ti–Cl(1)	2.236 (1)	O(1)–C(1)	1.427 (4)
Ti–Cl(2)	2.240 (1)	O(2)–C(12)	1.429 (4)
Ti–O(1)	1.738 (2)	C(5)–C(6)	1.333 (4)
Ti–O(2)	1.739(2)	C(3)–C(7)	1.326 (5)
Bond Angles			
Cl(1)–Ti–Cl(2)	110.34 (4)	Ti–O(1)–C(1)	154.6 (2)
Cl(1)–Ti–O(1)	111.33 (8)	Ti–O(2)–C(12)	153.0 (2)
Cl(1)–Ti–O(2)	110.71 (8)	C(3)–C(4)–C(5)	102.6 (3)
C(2)–C(3)–C(4)	109.8 (3)	C(4)–C(5)–C(6)	112.4 (3)

Results and Discussion

Cp*FvTiCl[8] (1) reacts with benzaldehyde in a 1:2 ratio, giving the yellow complex 2 in 47% yield (eq 1).

$$\underset{1}{\text{Cp*FvTiCl}} + 2\text{C(O)HPh} \rightarrow \underset{2}{\text{Cp*[(OCHPh)}_2\text{C}_5\text{Me}_4\text{(CH}_2\text{)]TiCl}} \quad (1)$$

When the reaction is carried out in a 1:1 ratio, half of the starting material remains unchanged, indicating that reaction with a second molecule of aldehyde is much faster than with the first.

Complex 2 was obtained as a yellow microcrystalline material. It is very air-sensitive and poorly soluble in toluene or pentane. It was characterized by IR and ^{1}H NMR spectroscopy and elemental analysis and identified as the dialkoxide Cp*Ti[(OCHPh)$_2$C$_5$Me$_4$(CH$_2$)]Cl. The exact geometry and bonding conformation of the modified fulvene ligand was confirmed by an X-ray crystal structure determination of a derivative (vide infra).

The dialkoxide ligand can be removed from the metal by treatment with HCl, which generates Cp*TiCl$_3$ and the free dialcohol 4 (eq 2).

$$\underset{2}{\text{Cp*[(OCHPh)}_2\text{C}_5\text{Me}_4\text{(CH}_2\text{)]TiCl}} + 2\text{HCl} \rightarrow \underset{3}{\text{Cp*TiCl}_3} + \underset{4}{\text{C}_5\text{Me}_4\text{(CH}_2\text{)(CHPhOH)}_2} \quad (2)$$

Treatment of 2 with TiCl$_4$ leads to formation of Cp*TiCl$_3$ and the titanium dialkoxide–dichloride complex 5 (eq 3).

$$2 + \text{TiCl}_4 \rightarrow \underset{3}{\text{Cp*TiCl}_3} + \underset{5}{\text{TiCl}_2\text{[(OCHPh)}_2\text{C}_5\text{Me}_4\text{(CH}_2\text{)]}} \quad (3)$$

Complex 5 was isolated as white crystals. It is very poorly soluble in pentane but dissolves reasonably well in toluene. A singlet at 61.21 ppm in the ^{13}C NMR spectrum of 5 indicates the presence of one or more sp^3 carbon atoms in the ring, while a triplet at low field [118.3 ppm ($^1J_{C-H}$ = 157.69 Hz)] unequivocally proves the existence of a =CH$_2$ group. All this indicates that the insertion has taken place somewhere in the ring instead of in the expected position, i.e., into the methylene–titanium bond.[2] Two singlets at 136.71 and 139.52 ppm are assigned to the remaining sp^2 carbon atoms in the ring. The NMR spectra of 2, 4, and 5 are relatively simple, and the small number of absorptions observed indicate a high symmetry of the new ligand. ^{1}H NMR spectra of all three compounds also show similar characteristics, as can be expected for compounds having the same ligand, and confirm the interpretation of the ^{13}C NMR spectrum given above.

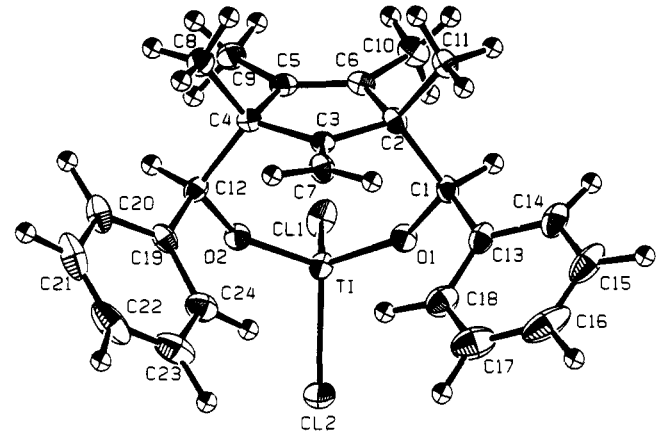

Figure 1. Molecular structure of Ti[(OCHPh)$_2$C$_5$Me$_4$(CH$_2$)]Cl$_2$ (5).

The molecular structure of 5 is shown in Figure 1. The complex is monomeric and shows a tetrahedral arrangement of the ligands around the titanium atom. Table I provides a selected list of pertinent bond distances and angles.

Ti–O(1) and Ti–O(2) distances (1.738 (2) and 1.739 (2) Å) together with the very obtuse Ti–O(1)–C(1) and Ti–O(2)–C(12) angles (154.6 (2) and 153.0 (2)°, respectively), indicate extensive π electron donation from oxygen to titanium.[9] In the same way the Ti–Cl(1) and Ti–Cl(2) distances (2.236 (1) and 2.240 (1) Å, respectively) also show some double-bond character, as expected for an electronically unsaturated complex.

The C$_5$ ring is practically planar (mean deviation from a plane is 0.008 Å) and has normal C–C distances for four single bonds (average 1.526 (4) Å) and one double bond (1.333 (4) Å). The exo double bond is also normal (1.326 (5) Å). Both features indicate that the five-membered ring has no interaction with the metal. The very long Ti–C distances Ti–C(7) = 4.548 (4) Å and Ti–C(3) = 3.664 (3) Å underline this conclusion. The two phenyl groups are both oriented in the same direction.

It is easier to understand the reaction if the starting material, Cp*FvTiCl, is formulated as a cis diene (structure C). Structure C can be seen as a close analogue of the well-known Cp*M(1,3-diene)X complexes reported before.[7] If structure C is a good description of the bonding in 1, then we can see the process as an insertion in both Ti–C σ-bonds.[10] Insertion after initial complexation of the aldehyde carbonyl oxygen atom to titanium will lead to attack on the fulvene ring plane from the metal side, thus explaining the observed stereoselectivity with respect to the configuration of the sp^3 ring carbon atoms.

The stereoselectivity of the aldehyde carbon atoms can be understood on the basis of steric arguments. It is reasonable to expect that insertion will take place in a manner in which the phenyl groups will be pointing away from the Cp* ligand. Once the dialkoxide ligand is formed, rotation around the C(C$_5$-ring)–C(alkyl) bond should be strongly obstructed.

The regioselectivity of attack in the fulvene ligand is not yet understood. Some mechanistic studies in order to clarify this point are in progress.

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Conclusions

We have shown that it is possible to transform a fulvene ligand into a dialkoxide with a specific geometry. Transfer of a Cp* ligand and replacement by a chloride ligand is quite possible, and this opens an interesting perspective for further derivatization and synthesis of new classes of compounds with challenging chemistry.

Experimental Section

General Remarks. All reactions were performed under nitrogen with use of Schlenk, glovebox, and vacuum-line techniques. Solvents were distilled from Na/K alloy prior to use; $CHCl_3$ and C(O)HPh were dried over molecular sieves (4 Å). IR spectra were recorded on a Pye-Unicam SP3-300 spectrophotometer using Nujol mulls between KBr disks. NMR spectra were recorded on a Bruker WH-90 or a Varian VXR-300 spectrometer. Chemical shifts are reported in parts per million and referenced to residual proton signals of the solvent (^{1}H: benzene-d_6, δ 7.15; chloroform-d, δ 7.24) or the solvent itself (^{13}C: benzene-d_6, δ 128.00; chloroform, δ 70.00). Elemental analyses were carried out at the Micro-Analytical Department of the University of Groningen. All data given are the average of two independent determinations.

Reaction of Cp*FvTiCl with C(O)HPh. To a solution of Cp*FvTiCl (0.4 g, 1.13 mmol) in 10 mL of toluene at 50 °C was added 0.23 mL (2.25 mmol) of benzaldehyde. The mixture was stirred for 2 h, and the resultant yellow precipitate, **2**, was separated and washed first with toluene/pentane and then with pentane; yield 0.30 g (0.53 mmol, 47%). IR (cm^{-1}): 3075 (w), 3020 (w), 1635 (w), 1600 (w), 1485 (w), 1240 (w), 1230 (w), 1200 (m), 1103 (vs), 1089 (vs), 1065 (s), 1050 (vs), 1020 (s), 940 (w), 908 (m), 880 (w), 795 (m), 768 (s), 738 (s), 728 (m), 700 (vs), 620 (w), 630 (w), 530 (w), 500 (w), 445 (m), 412 (s), 402 (s). Anal. Calcd for $TiClO_2C_{34}H_{41}$: C, 72.27; H, 7.31; Ti, 8.47; Cl, 6.27. Found: C, 72.22; H, 7.10; Ti, 8.40; Cl, 6.26. ^{1}H NMR (δ, benzene-d_6, 90 MHz, 20 °C): 0.83 (s, 6 H, Me), 1.88 (s, 6 H, Me), 1.98 (s, 15 H, Cp*), 4.70 (s, 2 H, $=CH_2$), 5.47 (s, 2 H, H—C—O), 7.25–7.48 (m, 10 H, Ph).

Reaction of 2 with HCl. To a suspension of **2** (0.1 g, 0.17 mmol) in 7 mL of $CHCl_3$ was added 0.1 mL of a solution of HCl (3.6 M) in Et_2O. The mixture turned orange immediately, and after the solvent was removed under vacuum, the product was analyzed by IR and ^{1}H and ^{13}C NMR measurements, which showed that it was a 1:1 mixture of compounds **3** and **4**. IR (cm^{-1}): 3225 (br), 1639 (w), 1600 (w), 1205 (w), 1114 (w), 1090 (w), 1050 (s), 1030 (s), 917 (m), 770 (m), 706 (vs), 621 (m), 466 (s). ^{1}H NMR (δ, benzene-d_6, 300 MHz): dialcohol $[C_5Me_4(CH_2)(CHPhOH)_2]$ 0.85 (s, 6 H, Me), 1.57 (s, 6 H, Me), 4.07 (s, 2 H, $=CH_2$), 4.48 (s, 2 H, H—C—O), 5.75 (s, 2 H, O—H), 7.15–7.35 (m, 10 H, Ph); Cp^*TiCl_3 1.89 (s, 15 H, Cp*). ^{13}C NMR (δ, benzene-d_6, 75.4 MHz): dialcohol $[C_5Me_4(CH_2)(CHPhOH)_2]$ 10.06 (q, $^1J_{C-H}$ = 125.46 Hz, C—Me), 26.79 (q, $^1J_{C-H}$ = 127.76 Hz, C—Me), 57.58 (s, C—C), 77.71 (d, $^1J_{C-H}$ = 142.73 Hz, H—C—O), 115.90 (t, $^1J_{C-H}$ = 156.54 Hz, $=CH_2$), 127.01 (d, $^1J_{C-H}$ = 158.84 Hz, Ph), 127.11 (d, $^1J_{C-H}$ = 161.14 Hz, Ph), 128.89 (d, $^1J_{C-H}$ = 151.85 Hz, Ph), 137.36 (s, C—Me), 142.14 (s, C—Me), 154.18 (s, α-Ph); Cp^*TiCl_3 14.05 (q, $^1J_{C-H}$ = 128.91 Hz, Me), 135.85 (s, C—Me).

Reaction of 2 with $TiCl_4$. To a suspension of **2** (0.29 g, 0.51 mmol) in 15 mL of $CHCl_3$ was added 54 μL (0.49 mmol) of $TiCl_4$, yielding an orange solution. The solvent was pumped off, and after several recrystallizations from toluene/pentane 0.12 g (0.25 mmol, 50%) of **5** was obtained as white crystals. IR (cm^{-1}): 3090 (w), 3030 (w), 1495 (w), 1305 (w), 1240 (w), 1200 (w), 1110 (sh), 1100 (s), 1090 (s), 1050 (vs), 1030 (s), 916 (m), 870 (w), 795 (w), 778 (m), 765 (s), 740 (s), 730 (sh), 708 (vs), 638 (w), 620 (w), 540 (w), 468 (vs), 409 (s). Anal. Calcd for $TiCl_2O_2C_{24}H_{26}$: C, 61.95; H, 5.63; Ti, 10.29; Cl, 15.23. Found: C, 61.59; H, 5.56; Ti, 10.30; Cl, 15.20. ^{1}H NMR (δ, chloroform-d, 300 MHz): 1.05 (s, 6 H, C—Me), 1.81 (s, 6 H, C—Me), 3.97 (s, 2 H, H—C—O), 5.53 (s, 2 H, $=CH_2$), 7.30 (m, 10 H, Ph). ^{13}C NMR (δ, chloroform-d, 75.4 MHz): 10.36 (q, $^1J_{C-H}$ = 125.46 Hz, C—Me), 25.61 (q, $^1J_{C-H}$ = 127.76 Hz, C—Me), 61.21 (s, C—C—O), 101.28 (d, $^1J_{C-H}$ = 149.64 Hz, H—C—O), 118.23 (t, $^1J_{C-H}$ = 157.69, $=CH_2$), 127.40 (d, $^1J_{C-H}$ = 159.99 Hz, Ph), 127.46 (d, $^1J_{C-H}$ = 159.99 Hz, Ph), 128.12 (d, $^1J_{C-H}$ = 160.00 Hz, Ph), 136.71 (s, C—Me), 139.52 (s, C—Me), 151.44 (s, α-Ph).

Crystal Structure Analysis. Crystal Data: $C_{24}H_{26}Cl_2O_2Ti$, M_r = 465.3, monoclinic, space group $P2_1/n$ ($P2_1/c$, nonstandard setting), a = 10.602 (5) Å, b = 14.157 (4) Å, c = 15.274 (5) Å, β = 103.76 (3)°, V = 2227 (1) Å^3, Z = 4, D_{calcd} = 1.39 g cm^{-3}, μ(Mo Kα) = 6.38 cm^{-1}.

Suitable colorless, irregular-shaped prisms were obtained by slow diffusion of pentane into a saturated solution of **5** in toluene. A crystal with the approximate dimensions 0.22 × 0.15 × 0.10 mm was mounted in epoxy resin on a glass fiber and transferred to a Rigaku AFC6R diffractometer. Diffracted intensities ($+h,+k,\pm l$) were measured at −150 ± 1 °C, with use of graphite-monochromated Mo Kα radiation from an RU200 rotating anode operated at 9 kW (50 kV; 180 mA). The $\omega/2\theta$ scan mode was employed for $3.5 < 2\theta < 50$ ° with an ω scan rate of 8° min^{-1} and a scan width of $(1.31 + 0.30 \tan\theta)$°. Weak reflections ($F < 10\sigma(F)$) were rescanned up to three times and counts accumulated to improve counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time vs background counting time was 2:1. Of the 3914 independent reflections measured, excluding those systematically absent, 2686 had $I > 3\sigma(I)$ and were regarded as being observed. That the crystal was not subject to decay during measurement of intensities was checked by monitoring three reflections at regular intervals (after measurements of 150 reflections). Intensity data were corrected for Lorentz and polarization effects, but no correction was made for the effects of absorption. Unit-cell parameters were obtained from diffractometer setting angles for 25 reflections in the range $44.6° < 2\theta < 48.7°$.

Structure Determination and Refinement. The structure was solved by direct methods (MITHRIL)[11] and subsequent electron density calculations. Full-matrix least-squares refinement of positional and anisotropic thermal parameters for the non-hydrogen atoms, with the hydrogen atoms as a fixed contribution in positions as located from a difference map, gave a final R = 0.037, R_w = 0.042, for 262 parameters and 2686 reflections. Atomic scattering factors and anomalous dispersion corrections were taken from ref 12, and the F_o values were weighted according to $w = [\sigma^2(F_o)]^{-1}$. A final difference map showed maximum and minimum residual densities of 0.47 and −0.29 e Å^{-3}, respectively. All calculations were carried out with the TEXSAN program system.[13]

Acknowledgment. We thank the Ministerio Español de Educacion y Ciencia for a postdoctoral fellowship for R.F.

Supplementary Material Available: Tables of bond lengths and angles, positional and thermal parameters, and least-squares planes for **5** (12 pages); a listing of observed and calculated structure factors for **5** (27 pages). Ordering information is given on any current masthead page.

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